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Free indium concentration determined with AGNES

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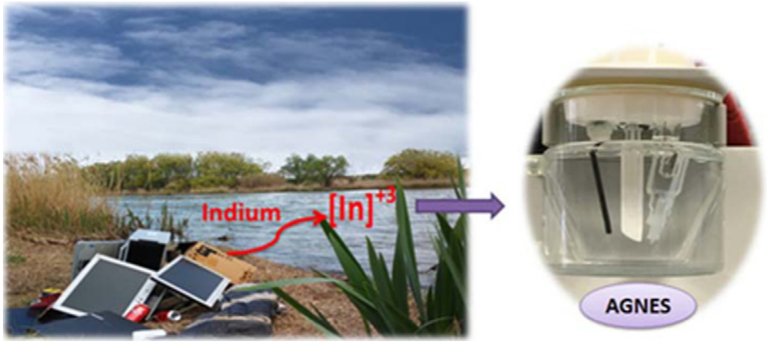
HIGHLIGHTS

- AGNES technique can measure free indium concentrations in aqueous solutions.
- A specific calibration procedure has been developed for indium.
- NIST46.6 stability constant values for In-complexes with oxalate or NTA are not optimal.
- High lability and mobility of In-oxalate complexes lead to fast measurements.

GRAPHICAL ABSTRACT



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ABSTRACT

Indium is increasingly used in electronic devices, from which it can be mobilized towards environmental compartments. Speciation of In in waters is important for its direct ecotoxicological effects, as well as for the fate of this element in the environment (e.g. fluxes from or towards sediments). Free indium concentrations in the environment can be extremely low due to hydrolysis, especially important in trivalent cations, to precipitation and to complexation with different ligands. In this work, the free indium concentration (which is a toxicologically and geochemically relevant fraction) in aqueous solutions at pH 3 has been measured with an adapted version of the electroanalytical technique AGNES (Absence of Gradients and Nernstian Equilibrium Stripping). Speciation measurements in mixtures of indium with the ligands NTA (nitrilotriacetic acid) and oxalate indicate that the values of their stability constants in the NIST46.6 database are less adequate than those published in some more recent literature. The extraordinary lability and mobility of In-oxalate complexes allow the measuring of free indium concentrations below nmol/L in just 25 s of deposition time.

1. Introduction

Ecotoxicological paradigms such as the Free Ion Activity Model (FIAM) or the Biotic Ligand Model (BLM) attribute a key role to the free metal ion concentration (or activity) (Paquin et al., 2002). Suitable analytical methods are therefore needed, for a variety of elements, to target this specific fraction of their total concentration.

Indium is a critical element present in a huge number of electronic devices (Abbas and Amer, 2013; Chung and Lee, 2012; Wood and Samson, 2006), from which it will eventually leach towards environmental waters and other compartments (White and Hemond, 2012; Zimmermann et al., 2013). To understand these fluxes from the anthroposphere to the hydrosphere, lithosphere and biosphere, the relevant chemical properties of this poorly-studied element have to be adequately elucidated. For instance, the large hydrolysis processes of indium (e.g. an increase by 0.1 units in the pH of a solution in equilibrium with precipitated $In(OH)_3$ decreases the free concentration by a

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factor of 2) are key to explain the transfer from some natural waters to the sediments (Nosal-Wiercinska, 2010; White et al., 2017). Moreover, hydrolysis also hinders the accurate study of its speciation with most conventional techniques and, so, there are many unresolved aspects of the behaviour of indium in a number of systems (Chung and Lee, 2012; Tuck, 1983). In particular, values of the reported stability constants of indium with most ligands are remarkably uncertain (Tuck, 1983).

Total indium concentrations in natural waters have been reported to be, generally, extremely low. Using mass spectrometry, Alibo et al. (1998) reported total concentrations of indium in the Pacific and Atlantic oceans in the range of 0.06 to 0.15 pmol/kg and 0.6 to 1.5 pmol/kg respectively, while river and estuarine waters were in the range 0.01 to 15 pmol/kg. A recent review (White and Hemond, 2012) concluded concentrations of indium in oceans from 0.006 to 0.5 ng L^{-1} and from 0.13 to 15 pg L^{-1} for some freshwaters. The concentration of dissolved indium (White et al., 2017) could reach 6 to 29 μg L^{-1} in streams influenced by acid mine drainage (pH around 3).

Several proposals for measuring free indium concentrations (i.e. the free concentrations of the hexaaquo complex) have been reported, including Ion Selective Electrodes (Abbas and Amer, 2013; Gupta et al., 2010) or molecularly imprinted polymer sensors (Zhang et al., 2015), but their limit of quantification (around 10^{-7} mol L^{-1}) is still relatively modest.

AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) (Galceran et al., 2004) is an emerging electroanalytical technique designed to determine free metal ion concentrations in solutions. Specific studied systems with environmental interest include seawaters (Diaz-de-Alba et al., 2014; Galceran et al., 2007), estuarine waters (Pearson et al., 2016), river waters (Parat et al., 2015; Zavarise et al., 2010), dispersions of nanoparticles (Adam et al., 2014; David et al., 2012; Domingos et al., 2008; Mu et al., 2014; Vale et al., 2015), quantum dots (Domingos et al., 2011), clay minerals dispersions (Rotureau, 2014), extracts of soils (Chito et al., 2012), humic acids solutions (Companys et al., 2007; Puy et al., 2008), etc. (see recent review (Galceran et al., 2014)). Although solid electrodes of Bi and Au have been able to determine free concentrations of Pb (Rocha et al., 2015) and Cu (Domingos et al., 2016), respectively, the typical implementation of AGNES with mercury electrodes requires amalgamating elements such as Zn, Cd, Pb or Sn. Given that indium is also an amalgamating element with a negative standard redox potential, it can be tackled with AGNES and conventional Hg electrodes.

The aim of this work is to show how AGNES can measure free indium concentration, $[In^{3+}]$. For toxicological and geochemical studies, the free ion concentration is a very relevant (even if sometimes small) fraction of the total dissolved concentration. This is the first application of AGNES to a trivalent ion. pH 3 is chosen here to avoid any complication from hydrolysis (Nosal-Wiercinska, 2010; White et al., 2017), for which conflicting formation constants have been reported (Alekseev et al., 2013; Tuck, 1983). This pH is relevant for acid mine drainages where high In concentrations have been reported (Nosal-Wiercinska, 2010; White et al., 2017). Speciation capability will be assessed with a ligand (NTA, nitrilotriacetic acid) forming a relatively inert complex and another one (oxalate) forming a labile one. The system In + NTA is also interesting for its application, in radiodiagnostic medicine (Biver et al., 2008), as vector of isotopes In-111 and In-113 to transferrin (implying iron substitution).

2. Experimental

2.1. Reagents

Indium solutions were prepared by dilution from a 1000 mg L^{-1} stock solution (Fluka, indium standard for ICP). NTA and potassium oxalate monohydrate (both Fluka, analytical grade) were used as ligands. Potassium nitrate was used as the inert supporting electrolyte at 0.1 mol L^{-1} (for all experiments) and prepared from solid KNO_3 (Fluka, TraceSelect). KOH and HNO_3 0.1 mol L^{-1} (Fluka) were used to adjust the pH of the solutions.

Ultrapure water (Synergy UV purification system Millipore) was used in all experiments. Purified water-saturated N_2 (purity ≥ 99.999%) was used for deaeration and blanketing the solutions.

2.2. Instrumentation and procedures

Voltammetric measurements were carried out with Autolab PGSTAT10 and PGSTAT101 potentiostats attached to Metrohm 663 VA Stands. All experiments were performed using GPES 4.9.007 (Eco Chemie) and NOVA 1.11 (Metrohm Autolab) software.

The working electrode was a Metrohm Hanging Mercury Drop Electrode (HMDE). Glassy carbon was used as the auxiliary electrode and the reference electrode was double-junction Ag/AgCl/3 mol L^{-1} KCl with KNO_3 0.1 mol L^{-1} in the salt bridge. A glass jacketed cell was used in all the experiments and thermostated at 25.0 °C. A glass combined electrode (Crison, 5209) was attached to an Orion Dual Star ion analyzer (Thermo) and introduced in the cell to measure and, accordingly, control the pH.

Purging with N_2 was necessary not only to spare a large signal from oxygen reduction, but also to avoid dramatic pH increases close to the electrode surface which would lead to indium hydrolysis (Aguilar et al., 2013a; Statsyuk and Dergacheva, 1998).

Differential Pulse Polarography (DPP) was used to have an initial estimate of the (deposition) potential to be applied in AGNES for a desired gain (i.e. accumulation factor) compensating any drift from the reference electrode. For DPP experiments, the largest stand drop (labelled "3" which according to the catalogue corresponds to a radius $r_0 = 203$ μm) has been used in order to be able to apply an expression, valid for planar geometry, to the DPP peak potential (Bard and Faulkner, 2001; Galceran et al., 2004). For the "short" DPP variant the drop lifetime was $t_d = 0.1$ s, while for the "long" DPP was $t_d = 1$ s; the scan rate was 4.5 mV/s and 0.45 mV/s, respectively. In both DPPs, the typical initial potential was −0.4 V and the final potential was −0.6 V; a modulation amplitude of 49.95 mV and a pulse time $t_p = 50$ ms were applied.

To assess indium reversibility (i.e. the fast reaching of equilibrium conditions – ruled by Nernst equation – between In^0 and In^{3+} at the electrode surface) in the conditions of this work, Cyclic Voltammograms (CV) were performed between −0.1 V and −0.8 V with a scan rate of 10 mV/s. More details on the ancillary techniques (DPP and CV) and on AGNES can be found in the Supplementary Material (SM).

We faced some difficulties while we were doing the speciation measurements with indium. The capillar of the mercury drop electrode was blocked more often than usual and we had also some irreproducibilities.

2.3. AGNES principles applied to indium analysis

AGNES is a stripping technique with two stages: deposition (accumulation in the amalgam) and stripping.

The deposition stage in AGNES lasts until a special situation of equilibrium is reached. Two conditions must be met: i) the ratio (called gain, Y) between the concentration in the amalgam and the free ion concentration in the solution is ruled by Nernst equation:

$$Y = \frac{[In^0]}{[In^{3+}]} = \exp\left[-\frac{3F}{RT}(E_1 - E^{\circ\prime})\right] \tag{1}$$

where F is the Faraday constant, R the gas constant, T the temperature, E_1 is the applied deposition potential and $E^{\circ\prime}$ is the standard formal potential of the redox couple; and ii) there are no gradients in the concentration profiles of the involved species (e.g. no fluxes of In^0, In^{3+}). In the simplest variant for the deposition stage, denoted 1P (one pulse), the total duration of the deposition stage applying E_1 is t_1, whose last period